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6. AUTHOR(S)

D. Zeng, M. Hampden-Smith, T. M. Alam
A. L. Rheingold

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Departments of Chemistry and Chemical Engineering
Center for Micro-Engineered Ceramics
University of New Mexico
Albuquerque, NM 871318. PERFORMING ORGANIZATION
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Monomeric, five-coordinate bis(diethyldithiocarbamate)M(II)(trialkylphosphine) complexes, 1 (M=Zn, alkyl=Me), 2 (M=Zn, alkyl=Et), 3 (M=Cd, alkyl=Me), and 4 (M=Cd, alkyl=Et), have been synthesized by addition of trialkylphosphine ligands to toluene solutions of bis(diethyldithiocarbamate)M(II) (M=Zn, and Cd). The bidentate ligand, 1,2-bis(diethylphosphino)ethane (DEPE) reacted with bis(diethyldithiocarbamate)M(II) (M=Zn, and Cd) and a 1:1 mixture of [(Et₂NCS₂)₂Zn]₂[(Et₂NCS₂)₂Cd]₂ in toluene to form five-coordinate, dinuclear DEPE bridged complexes, [(Et₂NCS₂)₂M]₂(μ-DEPE), 5 (M=Zn), 6 (M=Cd) and 7 [(Et₂NCS₂)₂Zn](μ-Et₂PCH₂CH₂PEt₂)[Cd(Et₂NCS₂)₂], respectively. The composition and structure of all compounds was confirmed by elemental analyses, infra-red spectroscopy, ¹H, ¹³C(¹H) and ³¹P(¹H) nuclear magnetic resonance (NMR) and in selected cases by X-ray crystallography. The solid state structures of (Et₂NCS₂)₂ZnPMe₃(1) and (Et₂NCS₂)₂CdPEt₃(4) have been determined by single-crystal X-ray diffraction.

Thermogravimetric analysis (TGA) of compounds 1-3 showed that the PR₃ ligands dissociated prior to thermal decomposition. However, compound 4 exhibited a single weight loss to give crystalline CdS as determined by X-ray powder diffraction, electron diffraction and transmission electron microscopy. The homobimetallic species, 5 and 6 also decomposed to give ZnS and CdS, respectively while the heterobimetallic species, 7, thermally decomposed to give crystalline Zn_{0.5}S according to X-ray powder diffraction data.

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Technical Report #11

Synthesis and Characterization of Single-Source Molecular
Precursors to Binary Metal Supphides: Bis(Diethyldithiocarbamato)
M(II)Trialkylphosphine (M=Zn and Cd) Adducts

by

D. Zeng, M. Hampden-Smith, T. M. Alam
A. L. Rheingold

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Department of Chemistry and Center for Micro-Engineered Ceramics

University of New Mexico

Albuquerque, NM 87131.

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**SYNTHESIS AND CHARACTERIZATION OF SINGLE-SOURCE
MOLECULAR PRECURSORS TO BINARY METAL SULPHIDES:
BIS(DIETHYLDITHIOCARBAMATO)M(II)TRIALKYLPHOSPHINE (M =
Zn AND Cd) ADDUCTS**

D. Zeng, M. J. Hampden-Smith*, T. M. Alam

**Department of Chemistry and Center for Micro-Engineered Ceramics
University of New Mexico
Albuquerque, NM 87131**

and

**A.L. Rheingold
Department of Chemistry
University of Delaware
Newark, DE 19716**

*** To whom correspondence should be addressed.**

Abstract

Monomeric, five-coordinate bis(diethyldithiocarbamato)M(II)(trialkylphosphine) complexes, **1** (M = Zn, alkyl = Me), **2** (M = Zn, alkyl = Et), **3** (M = Cd, alkyl = Me), and **4** (M = Cd, alkyl = Et) have been synthesized by addition of trialkylphosphine ligands to toluene solutions of bis(diethyldithiocarbamato)M(II) (M = Zn, and Cd). The bidentate ligand, 1,2-bis(diethylphosphino)ethane (DEPE) reacted with bis(diethyldithiocarbamato)M(II) (M = Zn, Cd) and a 1:1 mixture of $[(Et_2NCS_2)_2Zn]_2$: $[(Et_2NCS_2)_2Cd]_2$ in toluene to form five-coordinate, dinuclear DEPE-bridged complexes, $[(Et_2NCS_2)_2M]_2(\mu-DEPE)$, **5** (M = Zn), **6** (M = Cd) and **7** $[(Et_2NCS_2)_2Zn](\mu-Et_2PCH_2CH_2PEt_2)[Cd(Et_2NCS_2)_2]$, respectively. The composition and structure of all compounds was confirmed by elemental analyses, infra-red spectroscopy, 1H , $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ nuclear magnetic resonance (NMR) spectroscopy and in selected cases by X-ray crystallography. Variable temperature $^{31}P\{^1H\}$ and $^{113}Cd\{^1H\}$ NMR showed that these complexes undergo a dynamic exchange process at room temperature involving M-P bond cleavage with activation parameters of $\Delta H^\ddagger = 9$ kcal/mol and $\Delta S^\ddagger = -7$ eu as determined by two independent measurements based on simulation of variable temperature $^{31}P\{^1H\}$ and $^{113}Cd\{^1H\}$ NMR data for **4**. The solid-state structures of $(Et_2NCS_2)_2ZnPMe_3$ (**1**) and $(Et_2NCS_2)_2CdPEt_3$ (**4**) have been determined by single-crystal X-ray diffraction. Compound **1** crystallized in the space group $P2_12_12$ with $a = 11.253$ (2) Å, $b = 12.613$ (2) Å, $c = 46.124$ (7) Å, $Z = 12$, $R = 5.76\%$ and $R_w = 7.09\%$ for 6842 independent reflections. Compound **4** crystallized in the space group $P2_1/c$ with $a = 11.389$ (2) Å, $b = 14.093$ (2) Å, $c = 15.446$ (2) Å, $\beta = 90.64$ (1)°, $Z = 4$, $R = 5.47\%$ and $R_w = 7.20\%$ for 4375 independent reflections. The single crystal X-ray diffraction structure of $[(Et_2NCS_2)_2Zn]_2(\mu-DEPE) \cdot 2C_7H_8$ (**5**) has been reported earlier and confirmed the dinuclear nature showing that the two zinc units were bridged by the DEPE ligand and not chelated.

Thermogravimetric analysis (TGA) of compounds 1 - 3 showed that the PR_3 ligands dissociated prior to thermal decomposition. However, compound 4 exhibited a single weight loss to give crystalline CdS as determined by X-ray powder diffraction, electron diffraction and transmission electron microscopy. The homobimetallic species, 5 and 6 also decomposed to give ZnS and CdS, respectively while the heterobimetallic species, 7, thermally decomposed to give crystalline $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ according to X-ray powder diffraction data.

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Introduction

The semiconductors, ZnS and CdS with band gaps of 3.68 eV and 2.42 eV,¹ respectively, are used widely in solar cell technology² as optical coatings due to their absorption characteristics³ in the UV and visible region of the electromagnetic spectrum. These materials also exhibit quantum-confinement effects which allow modification of their electronic structure as a function of size in the nanometer size regime.⁴⁻⁶ Thin films and powders of these materials have been prepared by chemical vapor deposition (CVD) and pyrolysis of inorganic or metal-organic precursors, respectively, using both separate metal and sulfur sources and single-source precursors. For CVD, the precursors must exhibit relatively high vapor pressure which requires that they have a low degree of aggregation and also ligands that are capable of reaction to produce uncontaminated films. Separate volatile metal and sulfur sources include dialkylzinc,^{3,7,8} dialkylcadmium^{7,8} compounds or their nitrogen donor adducts⁹⁻¹¹ or bis(neopentyl)cadmium (II)¹² in conjunction with H₂S or heterocyclic sulfur compounds.⁸ The major problems associated with these species as CVD precursors are the use of the toxic gas, H₂S, and the possibility of premature reaction between the two sources^{7,10,13} in the gas phase before reaching the substrate. Volatile single-source metal-organic precursors, in which the necessary elements are contained in a single molecule, have the advantages of the potential for better control over composition and homogeneity of the deposit and they avoid the use of toxic gases such as H₂S. Relatively few single-source precursors have been used for deposition of metal sulfide films via CVD, including bis(diethyldithiocarbamate)zinc and cadmium complexes^{14,15} and their alkyl substituted derivatives, [RM(E₂CNEt₂)]₂, (M = Zn, Cd; E = S, Se; R = Me, Et, *t*-Bu and neopentyl)¹⁶⁻¹⁸ The simple alkylthiolato Zn and Cd compounds, [M(SMe)₂]₂ (M = Zn and Cd),^{19,20} and the sterically hindered compounds, [Cd(EC₆H₂(-*t*-Bu)₃)₂]₂ (E = S, Se)^{21,22} mercaptobenzothiazolates, [Cd(C₅H₄NS₂)₂]_n,^{23,24} and dimethylthiophosphate compounds, M(S₂PMe₂)₂ are known, but have not been used for CVD.²⁵

The polymeric compounds, $[(\text{PhS})_2\text{M}]_2(\text{DEPE})_n$ ($\text{DEPE} = 1,2$ -bis(diethylphosphino)ethane, $\text{M} = \text{Zn}, \text{Cd}$ and Hg) and dimeric compounds, $[(\text{PhS})_2\text{M}(\text{DEPE})]_2$ ^{26,27} thermally decompose to form metal sulfide powders rather than films due to their low volatility and low thermal stability.

Volatility may be improved by limiting the degree of aggregation of these species using neutral donor ligands to remove vacant metal coordination sites. For example, the monomeric species, bis(diethyldithiocarbamato)zinc(II)(TMEDA), where TMEDA = tetramethylethylenediamine, was recently used as a precursor for formation of ZnS films via CVD, and ZnS powders via aerosol-assisted gas phase decomposition.²⁸ However, TGA data reveal that this compound thermally dissociates to evolve TMEDA prior to sublimation, with formation of dimeric $[(\text{Et}_2\text{NCS}_2)_2\text{Zn}]_2$. Although the monomeric nature $[(\text{Et}_2\text{NCS}_2)_2\text{Zn}]$ may be retained in the gas phase under certain conditions,²⁸ it would be valuable to identify monomeric bis(dialkyldithiocarbamato)zinc and cadmium adducts that are suitable precursors for the CVD of metal sulfide films, where a Lewis base is used to prevent oligomerization but which does not dissociate prior to sublimation. The dialkyldithiocarbamato ligand is a suitable choice for the formation of metal sulfides because it has been demonstrated that complexes of this ligand decompose cleanly to give the corresponding metal sulfide.^{29,30}

In this paper, we report the synthesis and characterization of a series of trialkylphosphine adducts of bis(diethyldithiocarbamato)zinc and cadmium complexes where the phosphorus atom is a soft base which we anticipated would render the M-P bond less thermally labile compared to amino ligands.³¹⁻³³ The dynamic behavior of the M-P bonds in solution as determined by variable temperature multinuclear NMR spectroscopy is described. The thermal stability of these complexes was investigated by thermogravimetric analysis under atmospheric pressure conditions to determine the suitability of these precursors for CVD.³⁴

Experimental Section

(i) **General Procedures.** Bis(diethyldithiocarbamato)zinc(II) (98%, Aldrich) was used as purchased, and bis(diethyldithiocarbamato)cadmium(II) (R. T. Vanderbilt) was purified prior to use by washing with toluene to remove the brownish soluble impurity. Trimethylphosphine and triethylphosphine were purchased from Aldrich Chemical Co, 1,2-bis(diethylphosphino)ethane was purchased from Strem Chemicals, Inc., and all the three phosphine ligands were used without further purification. All reactions were carried out under a dry dinitrogen atmosphere using standard Schlenk techniques.³⁵ Analytical data were obtained in the absence of an inert atmosphere. Toluene and pentane were dried and distilled from sodium benzophenone ketyl and stored over 4Å sized molecular sieves prior to use in all cases. Elemental analyses were performed on a Perkin-Elmer 2400 Elemental Analyzer in the Department of Chemistry at the University of New Mexico. NMR data were recorded on a Bruker AC-250 NMR spectrometer by using the protio impurity of the deuterated solvent as reference for ^1H NMR spectroscopy; the ^{13}C resonances of the solvent as reference for $^{13}\text{C}\{^1\text{H}\}$ and ^{13}C NMR spectroscopy; 85% phosphoric acid for $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and a 3.0M aqueous solution of cadmium sulfate ($\delta = 5.00$ ppm) for $^{113}\text{Cd}\{^1\text{H}\}$ NMR spectroscopy.³⁶ Typical experimental parameters include a spectral width of 3247 Hz, with 32K spectra using 8 scans and 1 second relaxation delay for ^1H NMR; a spectral width of 14286 Hz, with 64K spectra using 100 to 10000 scans and a 2 second relaxation delay for $^{13}\text{C}\{^1\text{H}\}$ NMR; a spectral width of 20000 Hz, with 64K spectra, 24 to 6000 scans with 2 second relaxation delay for $^{31}\text{P}\{^1\text{H}\}$ NMR and, spectral width of 11628 Hz, 32K spectra with 1000 to 20000 scans and 5 second relaxation delay for $^{113}\text{Cd}\{^1\text{H}\}$ NMR. The $^{31}\text{P}\{^1\text{H}\}$ 2D cosy was obtained by using 8 scans, 1K spectra and 256 experiments at 178 K. To aid the assignment of ^{13}C resonances, both ^1H coupled and decoupled spectra were obtained as detailed in the syntheses. Temperature was controlled

to $\pm 1^\circ\text{C}$ using liquid nitrogen boil off and a thermocouple previously calibrated using external standards. Infra-red data were recorded on a Perkin-Elmer Model 1620 FTIR spectrophotometer. Thermogravimetric analysis was performed on a Perkin-Elmer 7700 Thermogravimetric Analyzer. Transmission Electron Microscopy (TEM) with Electron Diffraction (ED) and Energy Dispersive Spectroscopy (EDS) were performed on a JEOL 2000-FX instrument operating at 200 KeV. X-ray powder diffraction data were collected on the PVD-V Scintag X-ray diffractometer using a smear mount method to load a uniform and thin layer of sample onto a piece of glass of size $3 \times 3 \text{ cm}^2$. Single-crystal X-ray diffraction data were collected on Siemens P4 Diffractometer by 2 θ scan (4 - 50 deg for both compound 1 and 4) using graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation.

(ii) **Syntheses.** One example of the synthetic procedure is given in detail and the characterization data are presented for other species formed by similar procedures.

a. Synthesis of Bis(diethyldithiocarbamato)zinc(II) trimethylphosphine (1): Bis(diethyldithiocarbamato)zinc(II) (1.81 grams, 5.00 mmole) was suspended in toluene (25 cm^3) and trimethylphosphine (0.76 gram, 10 mmole) was added by syringe while stirring at room temperature. Immediate dissolution of the starting material, bis(diethyldithiocarbamato)zinc(II) was observed. The mixture was stirred at room temperature for ~10 min. and then 50 cm^3 of pentane was added to form a white suspension. The suspension was cooled to -20°C overnight and yielded white precipitate. The precipitate was separated and dried with a N_2 flow and the product was identified as $(\text{Et}_2\text{NCS}_2)_2\text{Zn}(\text{PMe}_3)$, 2.05 grams, 94 % based on bis(diethyldithiocarbamato)zinc(II). Elemental analysis (%): Found: C, 35.63; H, 6.95; N, 6.36. Calcd for $\text{C}_{13}\text{H}_{29}\text{N}_2\text{S}_4\text{PZn}$: C, 35.65; H, 6.67; N, 6.40. IR (KBr disk, cm^{-1}): 2974 (s), 2932(s), 2905(w), 2871 (w), 1700 (w), 1653 (w), 1560 (w), 1488 (vs), 1456 (s), 1422 (vs), 1375 (s), 1356 (s), 1301 (s), 1271 (vs), 1208 (vs), 1142 (s), 1093 (m), 1073 (s), 996 (s), 947 (m), 914 (s), 842 (s), 780 (m), 740 (m), 669 (w), 607 (w), 566

(m), 504 (w), 465 (w) and 425 (w). ^1H -NMR (C_6D_6): 0.96 ppm (t, $^3J_{\text{H-H}} = 7.1$ Hz, 12 H, NCH_2CH_3), 0.98 ppm (d, $^2J_{\text{P-H}} = 6.0$ Hz, 9 H, PCH_3), 3.55 ppm (q, $^3J_{\text{H-H}} = 7.1$ Hz, 8 H, NCH_2CH_3) at 298 K. $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): 11.75 ppm (d, $^1J_{\text{P-C}} = 17.2$ Hz, PCH_3), 12.02 ppm (s, NCH_2CH_3), 48.59 ppm (s, NCH_2CH_3) and 203.77 ppm (s, NCS_2) at 298 K.

b. Bis(diethyldithiocarbamato)zinc(II) triethylphosphine (2): Yield = 92 %. Elemental analysis (%): Found: C, 40.12; H, 7.39; N, 5.58. Calcd for $\text{C}_{16}\text{H}_{35}\text{N}_2\text{S}_4\text{PZn}$: C, 40.03; H, 7.35; N, 5.84. IR (KBr disk, cm^{-1}): 2968 (s), 2933(s), 2908(m), 2875 (m), 1700 (w), 1654 (w), 1560 (w), 1488 (vs), 1457 (s), 1426 (vs), 1377 (m), 1356 (m), 1298 (m), 1269 (vs), 1209 (vs), 1141 (vs), 1121 (vs), 1098 (m), 1076 (s), 1042 (m), 995 (s), 913 (s), 841 (s), 784 (s), 769 (s), 742 (w), and 569 (m). ^1H -NMR (C_6D_6): 1.17 ppm (d x t, $^3J_{\text{P-H}} = 15.3$ Hz and $^3J_{\text{H-H}} = 7.7$ Hz, 9 H, PCH_2CH_3), 1.26 ppm (t, $^3J_{\text{H-H}} = 7.1$ Hz, 12 H, NCH_2CH_3), 1.81 ppm (overlapped d x q, $^2J_{\text{P-H}} = 7.4$ Hz and $^3J_{\text{H-H}} = 7.6$ Hz, 6 H, PCH_2CH_3), 3.86 ppm (q, $^3J_{\text{H-H}} = 7.1$ Hz, 8 H, NCH_2CH_3) at 298 K. $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_7D_8): 7.84 ppm (s, PCH_2CH_3), 12.13 ppm (s, NCH_2CH_3), 14.41 ppm (d, $^1J_{\text{P-C}} = 14.9$ Hz, PCH_2CH_3), 48.69 (s, NCH_2CH_3) and 203.64 ppm (s, NCS_2) at 298 K. $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_7D_8): -15.66 ppm (s) at 298K.

c. Bis(diethyldithiocarbamato)cadmium(II) trimethylphosphine (3): Yield = 91%. Elemental analysis (precipitate material)(%): Found: C, 31.95; H, 6.26; N, 5.79. Calcd for $\text{C}_{13}\text{H}_{29}\text{N}_2\text{S}_4\text{PCd}$: C, 32.19; H, 6.03; N, 5.78. Elemental analysis (recrystallized from toluene)(%): Found: C, 32.43; H, 6.23; N, 5.89. Calcd for $\text{C}_{13}\text{H}_{29}\text{N}_2\text{S}_4\text{PCd}$: C, 32.19; H, 6.03; N, 5.78. IR (KBr disk, cm^{-1}): 2973 (s), 2932(s), 2902(m), 2871 (w), 1700 (w), 1653 (w), 1559 (w), 1490 (vs), 1456 (s), 1422 (vs), 1375 (m), 1355 (s), 1300 (m), 1270 (vs), 1205 (vs), 1142 (s), 1093 (m), 1073 (s), 990 (s), 961 (m), 946 (w), 911 (s), 840 (m), 779 (w), 740 (w), 669 (w), 608 (w), 563 (m), 506 (w),

458 (w) and 425 (w). ^1H -NMR (C_6D_6): 0.89 ppm (d, $^2J_{\text{P-H}} = 6.2$ Hz, 9 H, PCH_3), 1.01 ppm (t, $^3J_{\text{H-H}} = 7.1$ Hz, 12 H, NCH_2CH_3), 3.62 ppm (q, $^3J_{\text{H-H}} = 7.1$ Hz, 8 H, NCH_2CH_3) at 298 K. $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): 12.04 ppm (s, NCH_2CH_3), 12.41 ppm (d, $^1J_{\text{P-C}} = 14.64$ Hz, PCH_3), 50.07 ppm (s, NCH_2CH_3) and 204.25 ppm (s, NCS_2) at 298 K. $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_7D_8): -46.26 ppm (s) at 298K, -45.93 ppm (s) at 266K, -45.08 ppm (s) at 231K, -43.75 ppm (s) at 195K and -42.71 ppm (s) at 172K.

d. Bis(diethyldithiocarbamate)cadmium(II) triethylphosphine (4):
Yield = 92% Elemental analysis (%): Found: C, 36.74; H, 6.79; N, 5.06. Calcd for $\text{C}_{16}\text{H}_{35}\text{N}_2\text{S}_4\text{PCd}$: C, 36.46; H, 6.69; N, 5.32. IR (KBr disk, cm^{-1}): 2969 (s), 2931(s), 2905(m), 2872 (m), 1701 (w), 1624 (w), 1561 (w), 1486 (vs), 1458 (s), 1419 (vs), 1373 (m), 1353 (s), 1302 (m), 1270 (vs), 1140 (vs), 1071 (s), 1044 (m), 990 (s), 912 (s), 840 (s), 770 (s), 750 (w), 732 (w), 696 (w), 606 (w), 564 (m) and 504 (w). ^1H -NMR (C_6D_6): 1.22 ppm (d x t, $^3J_{\text{P-H}} = 16.3$ Hz and $^3J_{\text{H-H}} = 7.7$ Hz, 9 H, PCH_2CH_3), 1.26 ppm (t, $^3J_{\text{H-H}} = 7.1$ Hz, 12 H, NCH_2CH_3), 1.84 ppm (overlapped d x q, $^2J_{\text{P-H}} = 7.5$ Hz and $^3J_{\text{H-H}} = 7.4$ Hz, 6 H, PCH_2CH_3), 3.88 ppm (q, $^3J_{\text{H-H}} = 7.1$ Hz, 8 H, NCH_2CH_3) at 298 K. $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_7D_8): 8.36 ppm (d, $^2J_{\text{P-C}} = 2.1$ Hz, PCH_2CH_3), 12.21 ppm (s, NCH_2CH_3), 15.58 ppm (d, $^1J_{\text{P-C}} = 11.4$ Hz, PCH_2CH_3), 49.93 (s, NCH_2CH_3) and 206.46 ppm (s, NCS_2) at 298 K. $^{31}\text{P}\{^1\text{H}\}$ -NMR (CD_2Cl_2): -6.45 ppm (s) at 328K, -6.38 ppm (s) at 318K, -6.19 ppm (s) at 298K, -6.10 ppm (s) at 284K, -6.03 ppm (s) at 272K, -6.04 ppm (s, br) at 261K, -5.85 ppm (s, br) at 249K, -5.82 ppm (s with br. satellite $^1J_{31\text{P-}^{111}\text{Cd}/^{113}\text{Cd}} = 1401.2$ Hz) at 237K, -5.74 ppm (s with br. satellite $^1J_{31\text{P-}^{111}\text{Cd}/^{113}\text{Cd}} = 1474.7$ Hz) at 225K, -5.62 ppm (s with satellites $^1J_{31\text{P-}^{111}\text{Cd}} = 1481.8$ Hz and $^1J_{31\text{P-}^{113}\text{Cd}} = 1549.5$ Hz) at 201K and -5.48 ppm (s with satellite $^1J_{31\text{P-}^{111}\text{Cd}} = 1506.2$ Hz and $^1J_{31\text{P-}^{113}\text{Cd}} = 1575.4$ Hz) at 178K. $^{113}\text{Cd}\{^1\text{H}\}$ -NMR (CD_2Cl_2): 402.4 ppm (s) at 328K, 404.1 ppm (s) at 318K, 407.5 ppm (s) at 298K, 408.9 ppm (s) at 284K, 410.0 ppm (s, br) at 272K, 407.4 ppm (s, br) at 261K, 414.4 ppm (d, br, $^1J_{^{113}\text{Cd-}^{31}\text{P}} =$

1356.3 Hz) at 249K, 415.8 ppm (d, br, $^1J_{113\text{Cd}-31\text{P}} = 1502.6$ Hz) at 237K, 416.7 ppm (d, $^1J_{113\text{Cd}-31\text{P}} = 1509.5$ Hz) at 225K, 419.3 ppm (d, $^1J_{113\text{Cd}-31\text{P}} = 1547.2$ Hz) at 201K and 421.5 ppm (d, $^1J_{113\text{Cd}-31\text{P}} = 1576.6$ Hz) at 178K.

e. Di[bis(diethyldithiocarbamato)Zn(II)] [μ -1,2-bis(diethylphosphino)ethane] (5): Yield = 92% yield based on bis(diethyldithiocarbamato)zinc(II). Elemental analysis (%), Found: C, 47.72; H, 7.51; N, 5.03. Calcd for $\text{C}_{44}\text{H}_{80}\text{N}_4\text{S}_8\text{P}_2\text{Zn}_2$: C, 47.42; H, 7.24; N, 5.03. IR (KBr disk, cm^{-1}): 2971 (s), 2931(s), 2911(m), 2873 (m), 1700 (w), 1653 (w), 1559 (w), 1490 (vs), 1457 (s), 1421 (vs), 1375 (m), 1355 (s), 1302 (m), 1271 (vs), 1208 (vs), 1144 (s), 1093 (m), 1074 (m), 1039 (w), 995 (vs), 914 (s), 842 (s), 778 (w), 764 (m), 733 (m), 696 (w), 605 (w), 567 (m), 505 (w), 467 9 (w) and 432 (w). ^1H -NMR (C_6D_6): 0.94 ppm (t, $^3J_{\text{H-H}} = 7.1$ Hz, 24 H, NCH_2CH_3), 1.10 ppm (d x t, $^3J_{\text{P-H}} = 14.94$ Hz, $^3J_{\text{H-H}} = 7.5$ Hz, 12 H, PCH_2CH_3), 1.68 ppm (m, br, 8 H, PCH_2CH_3), 2.10 ppm (s, 6 H, $\text{C}_6\text{H}_5\text{CH}_3$), 2.16 ppm (s, br, 4 H, CH_2PEt_2), 3.52 ppm (q, $^3J_{\text{H-H}} = 7.1$ Hz, 16 H, NCH_2CH_3), 6.99 - 7.13 ppm (m, 10 H, $\text{C}_6\text{H}_5\text{CH}_3$) at 298 K. ^{13}C -NMR (CDCl_3): 7.86 ppm (q x t, $^1J_{\text{C-H}} = 128.2$ Hz, $^2J_{\text{C-H}} = 4.3$ Hz, PCH_2CH_3), 12.13 ppm (q x t, $^1J_{\text{C-H}} = 127.6$ Hz, $^2J_{\text{C-H}} = 3.1$ Hz, NCH_2CH_3), 14.78 ppm (overlapped d x d, $^4J_{\text{P-C}} = 6.9$ and $^1J_{\text{P-C}} = 7.4$ Hz when ^1H decoupled, m when ^1H coupled, PCH_2CH_3), 17.19 ppm (overlapped d x d, $^2J_{\text{P-C}} = 7.9$ and $^1J_{\text{P-C}} = 7.4$ Hz when ^1H decoupled, m when ^1H coupled, CH_2PEt_2), 21.40 ppm (q, $^1J_{\text{C-H}} = 127.3$ Hz, $\text{C}_6\text{H}_5\text{CH}_3$), 48.74 ppm (t x q $^1J_{\text{C-H}} = 139.2$ Hz, $^2J_{\text{C-H}} = 3.7$ Hz, NCH_2CH_3), 125.23, 128.16, 128.97 and 137.80 ppm (m, $\text{C}_6\text{H}_5\text{CH}_3$), 203.42 ppm (p, $^3J_{\text{C-H}} = 4.9$ Hz, CH_2NCS_2) at 298 K. $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_7D_8): -15.01 ppm (s) at 298K, -15.41 ppm (s) at 237K, -15.26 ppm (s) at 178K.

f. Di[bis(diethyldithiocarbamato)Cd(II)] [μ -1,2-bis(diethylphosphino) ethane] (6): Yield = 86%. Elemental analysis (%), Found: C, 34.94; H,

6.95; N, 5.30 and C, 35.56; H, 6.87; N, 5.41. Calcd for $C_{30}H_{64}N_4S_8P_2Cd_2$: C, 35.18; H, 6.29; N, 5.47. IR (KBr disk, cm^{-1}): 2969 (s), 2931(s), 2906(m), 2873 (m), 1701 (w), 1654 (w), 1561 (w), 1490 (vs), 1456 (s), 1420 (vs), 1376 (s), 1354 (s), 1302 (m), 1271 (vs), 1207 (vs), 1144 (vs), 1115 (w), 1090 (m), 1074 (s), 990 (vs), 913 (s), 841 (s), 779 (w), 762 (s), 730 (w), 679 (w), 608 (w), 564 (m) and 505 (w). 1H -NMR ($CDCl_3$): 1.28 ppm (d x t, $^3J_{P-H} = 15.46$ Hz, $^3J_{H-H} = 7.7$ Hz, 12 H, PCH_2CH_3), 1.35 ppm (t, $^3J_{H-H} = 7.1$ Hz, 24 H, NCH_2CH_3), 1.97 ppm (m, br, 8 H, PCH_2CH_3), 2.31 ppm (s, br, 4 H, CH_2PEt_2), 2.41 ppm (s, 6 H, $C_6H_5CH_3$), 3.95 ppm (q, $^3J_{H-H} = 7.1$ Hz, 16 H, NCH_2CH_3), 7.21 - 7.34 ppm (m, 10 H, $C_6H_5CH_3$) at 298 K. ^{13}C -NMR ($CDCl_3$): 8.28 ppm (q x t, $^1J_{C-H} = 128.2$ Hz, $^2J_{C-H} = 4.3$ Hz, PCH_2CH_3), 12.12 ppm (q x t, $^1J_{C-H} = 127.6$ Hz, $^2J_{C-H} = 3.1$ Hz, NCH_2CH_3), 15.66 ppm (overlapped d x d, $^4J_{P-C} = 6.1$ and $^1J_{P-C} = 6.1$ Hz when 1H decoupled, m when 1H coupled, PCH_2CH_3), 18.50 ppm (overlapped d x d, $^2J_{P-C} = 8.0$ and $^1J_{P-C} = 8.0$ Hz when 1H decoupled, m when 1H coupled, CH_2PEt_2), 21.42 ppm (q, $^1J_{C-H} = 127.0$ Hz, $C_6H_5CH_3$), 49.97 ppm (t x q $^1J_{C-H} = 138.6$ Hz, $^2J_{C-H} = 3.7$ Hz, NCH_2CH_3), 125.23, 128.18, 128.99 and 137.83 ppm (m, $C_6H_5CH_3$), 204.40 ppm (p, $^3J_{C-H} = 4.9$ Hz, CH_2NCS_2) at 298 K. $^{31}P\{^1H\}$ -NMR (C_7D_8): -7.45 ppm (s) at 298K, -7.38 ppm (s) at 251K, -7.51 ppm (s) at 204K, -7.75 ppm (s with satellite $^1J_{31P-111Cd} = 1452.3$ Hz, $^1J_{31P-113Cd} = 1519.7$ Hz and $^4J_{31P-111/113Cd} = 39.3$ Hz) at 178K.

g. Bis(diethyldithiocarbamato)Zn(II)[μ -1,2-bis(diethylphosphino)ethane]bis(diethyldithiocarbamato)Cd(II) (7): Yield = 96 % yield. This compound was dried *in vacuo* at 10^{-2} torr at room temperature to obtain the toluene free white powder $[(Et_2NCS_2)_2Zn_{0.5}/Cd_{0.5}]_2(Et_2PCH_2CH_2PEt_2)$. Elemental analysis (%), Found for the crystal product with toluene: C, 44.47; H, 7.37; N, 4.87. Calcd $C_{44}H_{80}N_4S_8P_2ZnCd$: C, 45.50; H, 6.94; N, 4.82. Found for toluene free white powder,: C, 36.84; H, 7.09; N, 5.73. Calcd $C_{30}H_{64}N_4S_8P_2ZnCd$: C, 36.88; H, 6.60;

N, 5.73. IR (KBr disk, cm^{-1}): 2972 (s), 2931(s), 2907(m), 2874 (m), 1701 (w), 1654 (w), 1561 (w), 1488 (vs), 1457 (s), 1421 (vs), 1375 (s), 1354 (s), 1302 (s), 1271 (vs), 1208 (vs), 1143 (vs), 1112 (w), 1091 (m), 1075 (m), 993 (vs), 913 (s), 842 (s), 780 (w), 765 (s), 731 (m), 695 (w), 607 (w), 565 (m) and 506 (w). ^1H -NMR (CDCl_3): 1.20 ppm (d x t, $^3\text{J}_{\text{P-H}} = 15.40$ Hz, $^3\text{J}_{\text{H-H}} = 7.7$ Hz, 12 H, PCH_2CH_3), 1.27 ppm (t, $^3\text{J}_{\text{H-H}} = 7.1$ Hz, 24 H, NCH_2CH_3), 1.86 ppm (m, br, 8 H, PCH_2CH_3), 2.15 ppm (s, br, 4 H, CH_2PEt_2), 2.33 ppm (s, 6 H, $\text{C}_6\text{H}_5\text{CH}_3$), 3.87 ppm (q, $^3\text{J}_{\text{H-H}} = 7.1$ Hz, 16 H, NCH_2CH_3), 7.13 - 7.24 ppm (m, 10 H, $\text{C}_6\text{H}_5\text{CH}_3$) at 298 K. ^{13}C -NMR (CDCl_3): 8.08 ppm (q x t, $^1\text{J}_{\text{C-H}} = 127.6$ Hz, $^2\text{J}_{\text{C-H}} = 4.3$ Hz, PCH_2CH_3), 12.12 ppm (q x t, $^1\text{J}_{\text{C-H}} = 127.6$ Hz, $^2\text{J}_{\text{C-H}} = 3.1$ Hz, NCH_2CH_3), 15.27 ppm (overlapped d x d, $^4\text{J}_{\text{P-C}} = 6.1$ and $^1\text{J}_{\text{P-C}} = 6.7$ Hz when ^1H decoupled, m when ^1H coupled, PCH_2CH_3), 17.90 ppm (overlapped d x d, $^2\text{J}_{\text{P-C}} = 7.4$ and $^1\text{J}_{\text{P-C}} = 7.9$ Hz when ^1H decoupled, m when ^1H coupled, CH_2PEt_2), 21.40 ppm (m, $^1\text{J}_{\text{C-H}} = 126.3$ Hz, $\text{C}_6\text{H}_5\text{CH}_3$), 49.28 ppm (t x q $^1\text{J}_{\text{C-H}} = 139.2$ Hz, $^2\text{J}_{\text{C-H}} = 3.7$ Hz, NCH_2CH_3), 125.24, 128.16, 128.98 and 137.81 ppm ($\text{C}_6\text{H}_5\text{CH}_3$), 203.87 ppm (p, $^3\text{J}_{\text{C-H}} = 4.9$ Hz, CH_2NCS_2) at 298 K. $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_7D_8): -11.19 ppm (s) at 298K. $^{31}\text{P}\{^1\text{H}\}$ -NMR (CD_2Cl_2): -10.26 ppm (s) at 298K, -5.26 ppm (d, $^3\text{J}_{\text{P-P}} = 38.2$ Hz $\text{Zn-P-CH}_2\text{-CH}_2\text{-P-Cd}$), -5.54 ppm (s with two sets of Cd satellites, $^1\text{J}_{111\text{Cd},31\text{P}} = 1405.3$ Hz, $^1\text{J}_{113\text{Cd},31\text{P}} = 1548.7$ Hz and $^4\text{J}_{111/113\text{Cd},31\text{P}} = 39.3$ Hz, $\text{Cd-P-CH}_2\text{-CH}_2\text{-P-Cd}$, compound 6, -14.09 ppm (s, $\text{Zn-P-CH}_2\text{-CH}_2\text{-P-Zn}$, compound 5, and -14.25 ppm (d, $^3\text{J}_{\text{P-P}} = 38.2$ Hz, $\text{Zn-P-CH}_2\text{-CH}_2\text{-P-Cd}$) at 178K. Compounds with empirical formula $[(\text{Et}_2\text{NCS}_2)_2\text{Zn}]_{2x}[\text{DEPE}][\text{Cd}(\text{S}_2\text{CNEt}_2)_2]_{2(1-x)}$ where $x = 0.75$ and 0.25 were also prepared by this method.

(iii) NMR Line Shape Simulation. Experimental spectra were transferred from the Bruker NMR instrument using the software ZZNET.³⁷ Simulations of both the ^{31}P and ^{113}Cd exchange broadened NMR line shapes were obtained using a modified version of the program DNMR5,³⁸ allowing iterative fitting of experimental spectra. All

simulations were performed on a 386 Personal Computer, treating the systems as uncoupled multi-spin $I = 1/2$ exchanging systems. The ^{113}Cd spectra was treated as a equally populated two-site exchange whose separation is given by the $^1J_{^{113}\text{Cd}-^{31}\text{P}}$ coupling. Both the J-coupling and chemical shift (ν_{CS}) were found to be temperature (T) dependent.

$$^1J_{^{113}\text{Cd}-^{31}\text{P}} (\text{T}) (\text{Hz}) = -1.00\text{T} + 1755$$

$$\nu_{\text{CS}} (\text{T}) (\text{Hz}) = -5.34\text{T} + 24320$$

Temperature variation of the line width in absence of the exchange process was not observed. The effective concentration, and thus the resulting exchange rates were scaled for the natural abundance of ^{113}Cd .

To simplify the intermediate exchange rate simulations in the ^{31}P spectra, a three-site model was used in the simulation, for exchange between the $^{113}\text{Cd}/^{111}\text{Cd}$ satellites in the ^{31}P spectra and the central transition corresponding to ^{31}P attached to ^{106}Cd , ^{108}Cd , ^{110}Cd , ^{112}Cd and ^{114}Cd . The resulting Eyring plots using the exchange rates obtained from the ^{113}Cd and ^{31}P simulations enabled the enthalpy of activation ΔH^\ddagger and entropy of activation ΔS^\ddagger to be determined.

(iv) **Single-Crystal X-ray Diffraction Data Collection.** Crystals that were suitable for X-ray single crystal diffraction data collection were obtained by recrystallization in toluene and pentane solution, and were mounted in capillary tubes for the data collection. Photographic evidence revealed *mmm* and *2/m* Laue symmetry for compounds 1 and 4 respectively. Systematic absences in the diffraction data allowed unique assignment of their space groups. No correction for absorption was required; the variation in transmission in ψ -scan data was less than 10% in both cases. Both structures were solved by heavy-atom methods and were refined with all non-hydrogen atoms

anisotropic. Hydrogen atoms were treated as idealized contributions. For **1**, the asymmetric unit consists of three crystallographically independent molecules which differ primarily in the conformations of the ligand ethyl groups. A Roger's test was used to determine the correct hand for **1**; $\eta = 1.07(5)$. All computations used the SHELXTL-PLUS library of programs (G. Sheldrick, Siemens XRD, Madison, WI). Crystallographic data are collected in Table 1. Atomic coordinates are available as supplementary materials. Bond lengths and angles are given in Table 2. The molecular structure of **4** is shown in Figure 3 as a representative example. Other figures are available as supplementary materials.

(v) **Thermogravimetric Analyses.** Samples of 10 to 25 mg of each compound were loaded into a platinum TGA pan while dry dinitrogen gas was flowing through the furnace tube. All TGA analyses were performed under the following conditions: temperature range; 50-600°C, heating rate; 20°C/min., ambient; dinitrogen gas at 1 atm. TGA data are tabulated in Table 4.

Results and Discussion

Synthesis and Characterization. Reactions of bis(diethyldithiocarbamate)M (II) (M = Zn or Cd) with one equivalent of the trialkylphosphines, PMe₃ or PEt₃ in toluene solution resulted in formation of adducts according to the stoichiometry of equation (1).



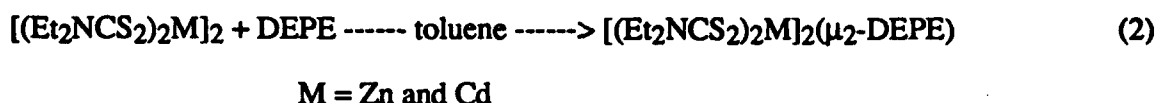
M = Zn and Cd

R = Me and Et

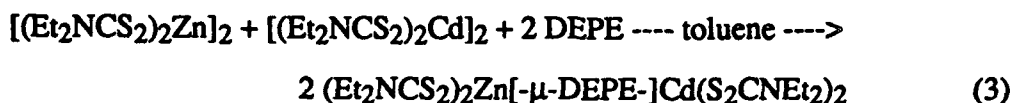
Reactions of $[(Et_2NCS_2)_2M]_2$ with PR_3 in 1:4 or 1:2 ratio generate the same products as shown in equation 1. It was not possible to form adducts with more than one PR_3 ligand coordinated to the metal center. Any excess uncoordinated PR_3 was removed during the filtration and washing with pentane. In the case of the reaction between $[(Et_2NCS_2)_2Zn]_2$ and PMe₃, the reaction was complete within a few seconds based on the rapid dissolution of the starting material, $[(Et_2NCS_2)_2Zn]_2$. However, when the solvent was removed at 10^{-2} torr, a white precipitate formed which was shown to be the starting material, $[(Et_2NCS_2)_2Zn]_2$, and not $(Et_2NCS_2)_2ZnPMe_3$ by ¹H-NMR spectroscopy and elemental analysis. This suggests that the Zn-P bond is labile in this compound. In general, reactions shown in equation (1) are essentially quantitative, with isolated yields of over 90% when pentane is used to precipitate the products. Recrystallization was not necessary to produce materials with satisfactory elemental analysis.

Earlier studies²⁸ showed that the chelating agent, tetramethylethylenediamine (TMEDA) reacts with half an equivalent of $[(Et_2NCS_2)_2Zn]_2$ in toluene solution to form a six-coordinate, distorted octahedral monomeric complex, $[(Et_2NCS_2)_2Zn(TMEDA)]$. Unfortunately, the TMEDA ligand dissociated from the metal center at low temperature

(onset temperature: 125°C) as determined by TGA studies.²⁸ This is consistent with data available for some other examples of N-donor adducts, $[(Et_2NCS_2)_2Zn(L)]$.³¹⁻³³ For comparison and in the hope of avoiding this problem, phosphorus-based chelating agents were investigated as part of this work. The compounds $[(Et_2NCS_2)_2M]_2$ ($M = Zn$ and Cd) were reacted with two equivalents of $Et_2PCH_2CH_2PEt_2$ (DEPE) in toluene solution. The reactions were complete in a few minutes at room temperature for $M = Cd$, and at 60°C for $M = Zn$. However, instead of forming a product with a chelating bidentate triorganophosphine ligand analogous to the species formed by reaction with TMEDA, the two phosphorus atoms bridged two metal centers to form a dinuclear compound according to equation (2).



In a separate experiment, a mixture of $[(Et_2NCS_2)_2Zn]_2$ and $[(Et_2NCS_2)_2Cd]_2$ in a 1:1 molar ratio was reacted with two equivalents of DEPE according to the stoichiometry shown in equation (3) in an attempt to prepare the mixed metal dinuclear species.



In all three cases, the products crystallized with two toluene molecules per dinuclear compound as shown by elemental analysis, 1H and ^{13}C NMR spectroscopy. Single-crystal X-ray diffraction structure determination confirmed this result and showed that the toluene molecules do not interact with the metal center.³⁹ As a result, the included toluene molecules can be removed easily, resulting in formation of a white, toluene-free powder. The facile removal of the toluene molecules resulted in inaccurate elemental analysis.

However, intentional removal of the toluene molecules completely, *in vacuo*, consistently yielded the toluene free product and gave accurate elemental analysis data.

All triorganophosphine adducts were characterized in solution and the solid-state by a number of different analytical techniques including NMR and IR spectroscopy and by single-crystal X-ray diffraction in representative cases. The very intense infra-red absorptions observed between 1488 - 1500 cm^{-1} were assigned to the C-N bond stretch and the bands at 990 - 996 cm^{-1} and 563 - 567 cm^{-1} to the asymmetric and symmetric $\nu(\text{C-S})$ bond stretches of the CS_2^- group. These assignments are consistent with the data for analogous compounds reported in the literature.^{16,17,28,40,41} In general, both symmetric and asymmetric C-S stretches are at a higher wavenumber for zinc compounds than for the analogous cadmium compounds. The absorptions found in the range 428 to 432 cm^{-1} may be assigned to the M-S bond stretches based on recent reports by O'Brien and co-workers.^{16,17}

The ^1H -NMR spectra for all monomeric compounds, $(\text{Et}_2\text{NCS}_2)_2\text{MPR}_3$ ($\text{M} = \text{Zn}$ and Cd , $\text{R} = \text{CH}_3$ and CH_2CH_3) exhibited integration ratios consistent with their empirical formulae. The corresponding ^{13}C NMR data were consistent with the ^1H -NMR results. In the case of the dinuclear species, **7**, formed by the reaction of equation 3, the $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts were approximately the average of those of compounds **5** and **6**. This observation does not distinguish between a physical mixture of the two compounds **5** and **6** in solution which undergo rapid exchange on the NMR timescale, and a single heterobimetallic species. Attempts to distinguish these possibilities are described later.

The variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for zinc compound **2** exhibited a singlet and were temperature invariant, but this does not distinguish whether or not these species undergo PR_3 exchange. In the case of the cadmium analogs, **3** and **4**, the room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra revealed a single chemical shift but without ^{111}Cd or ^{113}Cd satellites. However, on cooling a CD_2Cl_2 solution of **4** to low temperatures, the satellite spectra appeared (see Figure 1). The intensity of the satellites was consistent with

the natural abundance of ^{111}Cd and ^{113}Cd . The ratios of the coupling constants were consistent with the gyromagnetic ratios of the ^{31}P , ^{113}Cd and ^{111}Cd nuclei, confirming this assignment. The coupling constants at 178K, for compound 4, were $^1J_{^{113}\text{Cd}-^{31}\text{P}} = 1575$ Hz and $^1J_{^{111}\text{Cd}-^{31}\text{P}} = 1506$ Hz. The observed temperature variation of the ^{31}P spectra shown in Figure 1 are consistent with a dynamic exchange process that involves Cd-P bond cleavage and intermolecular exchange of PEt_3 between spin-active and non-spin-active Cd(II) centers. However, no Cd satellites were observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $(\text{Et}_2\text{NCS}_2)_2\text{CdP}(\text{CH}_3)_3$ even at 178K indicating a higher exchange rate (lower activation barrier) for this smaller phosphine ligand. In order to quantify this exchange process, the variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR of 4 were simulated and the exchange rate constants (k_{ex}) obtained. These rate constants represent the reversible first order reaction shown in equation 4 where Cd-P bond cleavage is proposed to be the rate-determining step.



An Eyring plot of $\ln(k_{\text{ex}}/T)$ versus reciprocal temperature⁴² gave the enthalpy of activation, $\Delta H^\ddagger = 9.8 \pm 0.2$ kcal/mol, and the entropy of activation, $\Delta S^\ddagger = -7 \pm 1$ eu. Although the dissociation of the compound 4 might be expected to lead to an increase in disorder ($\Delta S^\ddagger > 0$), solvation effects may dominate and contribute to the increase in order.

To investigate this dynamic exchange process further, variable temperature $^{113}\text{Cd}\{^1\text{H}\}$ NMR spectra were also obtained for compound 4, $(\text{Et}_2\text{NCS}_2)_2\text{CdPEt}_3$ and are presented in Figure 2. The ^{113}Cd -NMR showed a single sharp resonance at high temperature which split into a doublet with a coupling constant consistent with the coordination to a single ^{31}P nucleus at lower temperature. At 178K, the coupling constant, $^1J_{^{31}\text{P}-^{113}\text{Cd}}$ is 1575 Hz. Simulation of the variable temperature ^{113}Cd NMR spectra yielded another set of rate constants (see Figure 2) as a function of temperature which were

used to calculate the activation parameters for the exchange process, allowing a comparison with the values obtained from the ^{31}P NMR simulation. The activation parameters ($\Delta H^\ddagger = 9 \pm 1$ kcal/mol and $\Delta S^\ddagger = -7 \pm 4$ eu) derived from the Eyring plot are consistent with those obtained from the $^{31}\text{P}\{^1\text{H}\}$ NMR simulations.

The homobimetallic species, **5** and **6**, exhibited singlets (-15.01 ppm for **5** and -7.45 ppm for **6**) in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in C_7D_8 at room temperature. For the Cd compound, **6**, no coupling to Cd was observed at room temperature, but one-bond and four-bond $^{111}/^{113}\text{Cd}$ - ^{31}P coupling satellites were obtained at 178K ($^1J_{^{113}\text{Cd}-^{31}\text{P}} = 1519.7.0$ Hz, $^1J_{^{111}\text{Cd}-^{31}\text{P}} = 1452.3$ Hz and $^4J_{^{111}/^{113}\text{Cd}-^{31}\text{P}} = 39.3$ Hz). The mixed metal products formed by the reaction of equation 3 also exhibited a singlet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at a chemical shift (-11.19 ppm) in C_7D_8 that was approximately the numerical average chemical shift of species **5** and **6** at room temperature. Again, this observation does not distinguish between the interpretations discussed above. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum obtained in CD_2Cl_2 at 178K is consistent with the presence of three species in solution. In the $^{31}\text{P}\{^1\text{H}\}$ spectra at 178K, there are two singlets consistent with the presence of compounds **5** and **6** and there is one pair of doublets at chemical shifts (one close to chemical shift of **5** and one close to chemical shift of **6**) consistent with the heterobimetallic species, $(\text{Et}_2\text{NCS}_2)_2\text{Zn}[\text{P}(\text{Et})_2\text{CH}_2\text{CH}_2(\text{Et}_2)\text{P}]\text{Cd}(\text{S}_2\text{CNEt}_2)_2$ (**7**). The doublet at -14.25 ppm ($^3J_{^{31}\text{P}-^{31}\text{P}} = 38.2$ Hz) was assigned to P coordinated to Zn, and doublet at -5.26 ppm assigned to P coordinated to Cd. A 2D $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift correlated experiment confirmed that the doublets were coupled to each other. In comparison, the 3-bond P-P coupling constant for the heterobimetallic compound through the P- CH_2CH_2 -P' chain is similar to the value reported for $\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}'_2$ species where R and R' are different.⁴³⁻⁴⁶ The presence of the 3-bond P-P coupling is consistent with the presence of the heterobimetallic compound **7** in this reaction mixture. The relative intensity of the three species in product as shown by equation 3 is approximately as

expected ($5:6:7 = 1:1:2$) for a statistical distribution of metal atom occupancy in all three compounds.

The structural integrity of the mixed metal species, **7** was investigated in the solid state by X-ray powder diffraction. The X-ray powder diffraction data for the heterobimetallic species **7** did not match that of either the homobimetallic species **5** or **6**. As a result we conclude that **7** is a homogeneous, heterobimetallic species in the solid state and not simply a physical mixture of **5** and **6**. However, on dissolution of **7**, a statistical distribution of all three compounds is observed as a result of the phosphine exchange process.

Solid-State Structural Data. Compounds **1**, **4** and **5** have been structurally characterized in the solid-state by single-crystal diffraction. Crystallographic data for **1** and **4** are collected in Table 1. Bond lengths and angles are given in Table 2. The molecular structure of **4** is shown in Figure 3 as a representative example. The structure of compound **5** was reported previously and shown to be a dinuclear species with the DEPE ligand bridging two five-coordinate bis(diethyldithiocarbamato)zinc (II) units.³⁹ This is somewhat surprising based on the observation that TMEDA chelates one zinc (II) center to form a monomeric compound $(\text{Et}_2\text{NCS}_2)_2\text{Zn}(\text{TMEDA})$.²⁸ In contrast, both $(\text{Et}_2\text{NCS}_2)_2\text{ZnPMe}_3$ and $(\text{Et}_2\text{NCS}_2)_2\text{CdPEt}_3$ are monomeric in the solid-state, exhibiting only chelating $\text{Et}_2\text{NCS}_2^-$ ligands. As is common in five-coordinate phosphine adducts of Zn and Cd complexes that contain chelating $\text{Et}_2\text{NCS}_2^-$ ligands, one M-S bond is significantly shorter (ca. 2.32 Å, M = Zn; 2.56 Å, M = Cd) compared to the other M-S bond (ca. 2.62 Å, M = Zn; 2.72 Å, M = Cd), see Table 3.⁴⁷ However, the monomeric, six-coordinate TMEDA chelating adduct does not show the bond length differences for both Zn-S and C-S bond. The localized nature of N-CS_2^- seems to be a general structural feature in five coordinate Zn and Cd system.

Thermogravimetric Analyses. Thermogravimetric analysis (Table 4) under one atmosphere of N_2 showed that M-P bonds are labile in the solid state for PMe_3 adducts, $(Et_2NCS_2)_2MPMe_3$ ($M = Zn$ for 1 and Cd for 3). Upon heating, the PMe_3 ligand dissociates from the metal center below $100^\circ C$ to liberate PMe_3 to form the starting material, " $(Et_2NCS_2)_2M$ " which exists as a dimer in the solid-state. Further heating results in sublimation of the dimer consistent with the TGA data for authentic $[(Et_2NCS_2)_2M]_2$. This interpretation was confirmed by comparing the X-ray powder diffraction data for " $(Et_2NCS_2)_2Cd$ " obtained by TGA of $(Et_2NCS_2)_2CdPMe_3$ with an authentic sample prepared by wet synthetic methods. The two powder patterns were identical. The observed PMe_3 weight losses for both compounds are usually less than the calculated ones. This was thought to be due to the ligand dissociation prior to TGA experiment. In fact, $(Et_2NCS_2)_2ZnPMe_3$ dissociates to form $[(Et_2NCS_2)_2Zn]_2$ and PMe_3 even at room temperature under vacuum. In the case of $(Et_2NCS_2)_2ZnPEt_3$ (2), TGA data shows that the Zn-P bond dissociation and sublimation of $[(Et_2NCS_2)_2Zn]_2$ occurred in a very narrow temperature regime but two steps are distinguishable. For compound 4, $(Et_2NCS_2)_2CdPEt_3$, TGA data shows a single step which corresponds to decomposition to form cadmium sulfide without sublimation. The residue was identified as crystalline hexagonal greenockite type cadmium sulfide by X-Ray powder diffraction data (Figure 4). The electron diffraction pattern (Figure 5) of this material is consistent with the X-ray diffraction data. The lattice fringes observed by TEM (Figure 5) have a d-spacing of 3.6 \AA , consistent with the X-ray diffraction and electron diffraction data. Energy dispersive spectroscopy showed the presence of Cd and S only. While the thermal decomposition of these precursors does lead to formation of the corresponding metal sulfide powders, it is important to investigate whether these compounds are sufficiently volatile for CVD purposes. Compound 4, $(Et_2NCS_2)_2CdPEt_3$, was heated *in vacuo*, 10^{-2} torr, and was observed to sublime completely. The use of these precursors for CVD to deposit metal sulfide films is currently being studied and will be reported separately.

The first weight loss for the dinuclear compounds is due to the loss of toluene molecules. If the toluene was removed prior to the TGA experiment, all the dinuclear compounds showed a single weight loss corresponding to the formation of the metal sulfide with release of the organic fragments. Bulk samples of compounds with empirical formula $[(Et_2NCS_2)_2Zn]_{2x}[DEPE][Cd(S_2CNEt_2)_2]_{2(1-x)}$ where $x = 1, 0.75, 0.50, 0.25$ and 0 were thermally decomposed under flowing N_2 gas at $450^\circ C$ for 30 minutes each. The resulting powders were analyzed by powder X-ray diffraction (Figure 6), and showed evidence for the formation of the following crystalline products, wurtzite phase ZnS, $Zn_{0.75}Cd_{0.25}S$, $Zn_{0.5}Cd_{0.5}S$, $Zn_{0.25}Cd_{0.75}S$ and CdS, respectively. The X-ray diffraction data were used for unit cell parameter refinement employing the Generalized Structure Analysis System (GSAS) by a least squares method. The space group for both ZnS and CdS is $P6_3mc$. Solid-solutions of these two materials have the same space group, thus in $Zn_xCd_{1-x}S$, both Zn and Cd have the same atomic coordinates and each atom contributes to the fractional occupancy (x for Zn and $1-x$ for Cd) of each metal position. A summary of the input (based on crystallographic data for ZnS and CdS) and refined unit cell parameters are presented in Table 5. After refinement, a new set of unit cell lengths, a and c were obtained. A plot of unit cell length versus composition showed that both a and c increased linearly with the increasing molar ratio of Cd/Zn, consistent with the Vegard's Law.⁴⁸

Summary and Conclusions

A series of compounds $(\text{Et}_2\text{NCS}_2)_2\text{MPR}_3$ where $\text{M} = \text{Zn}, \text{Cd}$ and $\text{R} = \text{Me}, \text{Et}$ have been prepared and characterized by a variety of spectroscopic techniques. Representative examples were shown to be monomeric in the solid state. That these species possess labile M-P bonds was demonstrated by variable temperature $^{31}\text{P}\{^1\text{H}\}$ and $^{113}\text{Cd}\{^1\text{H}\}$ NMR spectroscopy which for the case of compound 4, $(\text{Et}_2\text{NCS}_2)_2\text{CdPEt}_3$, revealed activation parameters of $\Delta H^\ddagger = 9 \text{ kcal/mol}$ and $\Delta S^\ddagger = -7 \text{ eu}$. The reaction of $[(\text{Et}_2\text{NCS}_2)_2\text{M}]_2$ with DEPE in all proportions investigated resulted in formation of DEPE bridged dinuclear complexes, $[(\text{Et}_2\text{NCS}_2)_2\text{M}]_2(\mu_2\text{-DEPE})$, rather than a mononuclear DEPE chelated complexes. Low temperature $^{31}\text{P}\{^1\text{H}\}$ NMR data of the product of the reaction between a 1:1 mixture of $[(\text{Et}_2\text{NCS}_2)_2\text{Zn}]_2 : [(\text{Et}_2\text{NCS}_2)_2\text{Cd}]_2$ with two equivalents of DEPE was consistent with formation of the heterobimetallic species $(\text{Et}_2\text{NCS}_2)_2\text{Zn}[\mu\text{-DEPE}]\text{Cd}(\text{S}_2\text{CNEt}_2)_2$ together with $[(\text{Et}_2\text{NCS}_2)_2\text{Cd}]_2(\mu_2\text{-DEPE})$ and $[(\text{Et}_2\text{NCS}_2)_2\text{Zn}]_2(\mu_2\text{-DEPE})$. At room temperature, all three species underwent a dynamic exchange process, probably involving intermolecular exchange of the DEPE ligand to give a single time-averaged $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift. In the solid-state, X-ray powder diffraction data were consistent with the presence of a homogeneous heterobimetallic species rather than a physical mixture of 5 and 6.

The TGA data of these compounds 1 - 3 under one atmosphere of N_2 revealed that they dissociate their PR_3 ligand prior to sublimation which is undesirable if these species are to be used as CVD precursors to produce metal sulfide films. However, compound 4 thermally decomposed in a single step to produce crystalline CdS. In addition, compound 4 sublimed quantitatively *in vacuo* and is a potential CVD precursor. The observed greater thermal instability of the $[(\text{Et}_2\text{NCS}_2)_2\text{M}]\text{PR}_3$ adducts in the order $\text{R} = \text{Me} > \text{R} = \text{Et}$ can be correlated with their dynamic solution NMR behavior. The homobimetallic and heterobimetallic species $[(\text{Et}_2\text{NCS}_2)_2\text{Zn}]_{2x}[\text{DEPE}][\text{Cd}(\text{S}_2\text{CNEt}_2)_2]_{2(1-x)}$ where $x = 1, 0.75, 0.50, 0.25$ and 0 thermally decomposed to form wurtzite phase ZnS, $\text{Zn}_{0.75}\text{Cd}_{0.25}\text{S}$,

$\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, $\text{Zn}_{0.25}\text{Cd}_{0.75}\text{S}$ and CdS , respectively. Further experiments are in progress to determine: (1) the conditions under which the reaction of bidentate phosphine ligands result in formation of chelates and (2) the suitability of these species to act as precursors for the CVD of metal sulfide films.

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Supplementary Materials: X-ray crystallographic data for $(\text{Et}_2\text{NCS}_2)_2\text{ZnPMe}_3$, Structure Determination Summary, Bond Lengths and angles, Anisotropic Displacement Coefficients, H-Atom Coordinates and Isotropic Displacement Coefficients (9 pages). X-ray crystallographic data for $(\text{Et}_2\text{NCS}_2)_2\text{CdPEt}_3$, Structure Determination Summary, Bond Lengths and angles, Anisotropic Displacement Coefficients, H-Atom Coordinates and Isotropic Displacement Coefficients (7 pages). Ordering information is given on any current masthead.

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List of Figure Captions

1. Comparison of Experimental (left) and simulated variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for compound 4, $(\text{Et}_2\text{NCS}_2)_2\text{CdPEt}_3$.
2. Comparison of Experimental (left) and simulated variable temperature $^{113}\text{Cd}\{^1\text{H}\}$ NMR spectra for compound 4, $(\text{Et}_2\text{NCS}_2)_2\text{CdPEt}_3$.
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Table 1. Crystallographic Data for:

a. $(\text{Et}_2\text{NCS}_2)_2\text{Zn}(\text{PMe}_3)$ Chemical Formula: $\text{C}_{13}\text{H}_{29}\text{N}_4\text{PS}_4\text{Zn}$, (1)

formula weight 438.0

 $a = 11.253 (2) \text{ \AA}$ space group $P2_12_12$ $b = 12.613 (2) \text{ \AA}$

Temp 231 K

 $c = 46.124 (7) \text{ \AA}$ $\lambda = 0.71073$ $V = 6547 (2) \text{ \AA}^3$ $\rho (\text{calc}) 1.333 \text{ g cm}^{-3}$ $Z = 12$ $\mu = 15.9$ $R(F), \% = 5.76$ $R(wF), \% = 7.09$ b. $(\text{Et}_2\text{NCS}_2)_2\text{Cd}(\text{PEt}_3)$.Chemical Formula: $\text{C}_{16}\text{H}_{35}\text{N}_4\text{PS}_4\text{Cd}$, (4)

formula weight 527.1

 $a = 11.389 (2) \text{ \AA}$ space group $P2_1/c$ $b = 14.093 (2) \text{ \AA}$

Temp 231 K

 $c = 15.446 (2) \text{ \AA}$ $\lambda = 0.71073$ $\beta = 90.64 (1) \text{ deg}$ $\rho (\text{calc}) = 1.412 \text{ g cm}^{-3}$ $V = 2478.9 (7) \text{ \AA}^3$ $\mu = 12.9$ $Z = 4$ $R(F), \% = 5.47$ $R(wF), \% = 7.20$

Table 2. Selected Bond Distances and Angles for $(\text{Et}_2\text{NCS}_2)_2\text{Zn}(\text{PMe}_3)$ and $(\text{Et}_2\text{NCS}_2)_2\text{Cd}(\text{PEt}_3)$.

	$(\text{Et}_2\text{NCS}_2)_2\text{Zn}(\text{PMe}_3)$			$(\text{Et}_2\text{NCS}_2)_2\text{Cd}(\text{PEt}_3)$
	mol. a	mol. b	mol. c	
(a) Bond Distances (Å)				
M-S(1)	2.328(5)	2.655(5)	2.618(5)	2.575(3)
M-S(2)	2.633(5)	2.329(4)	2.324(4)	2.715(2)
M-S(3)	2.321(4)	2.614(4)	2.616(4)	2.557(2)
M-S(4)	2.638(5)	2.327(4)	2.340(4)	2.723(2)
M-P	2.380(4)	2.379(4)	2.388(4)	2.573(3)
(b) Bond Angles (deg)				
S(1)-M-S(2)	72.0(1)	72.3(1)	72.6(1)	67.9(1)
S(1)-M-S(3)	125.7(2)	168.2(1)	168.9(1)	125.4(1)
S(1)-M-S(4)	100.4(2)	100.7(1)	104.0(2)	101.0(1)
S(2)-M-S(3)	105.8(1)	104.1(1)	101.0(1)	102.9(1)
S(2)-M-S(4)	169.6(1)	130.9(2)	130.4(2)	159.2(1)
S(3)-M-S(4)	72.6(1)	72.8(1)	72.9(1)	68.4(1)
P-M-S(1)	117.4(2)	90.2(1)	93.7(2)	114.5(1)
P-M-S(2)	99.1(2)	115.4(2)	121.4(2)	102.5(1)
P-M-S(3)	116.5(2)	101.4(2)	97.3(2)	120.0(1)
P-M-S(4)	90.7(2)	113.1(2)	108.2(2)	98.1(1)
(c) Dihedral Angle (deg)				
[M-C-S(1)-S(2)]- [M-C-S(3)-S(4)]	53.8	47.1	47.9	55.3

Table 3. Comparison of bond lengths (Å) and angles (°).

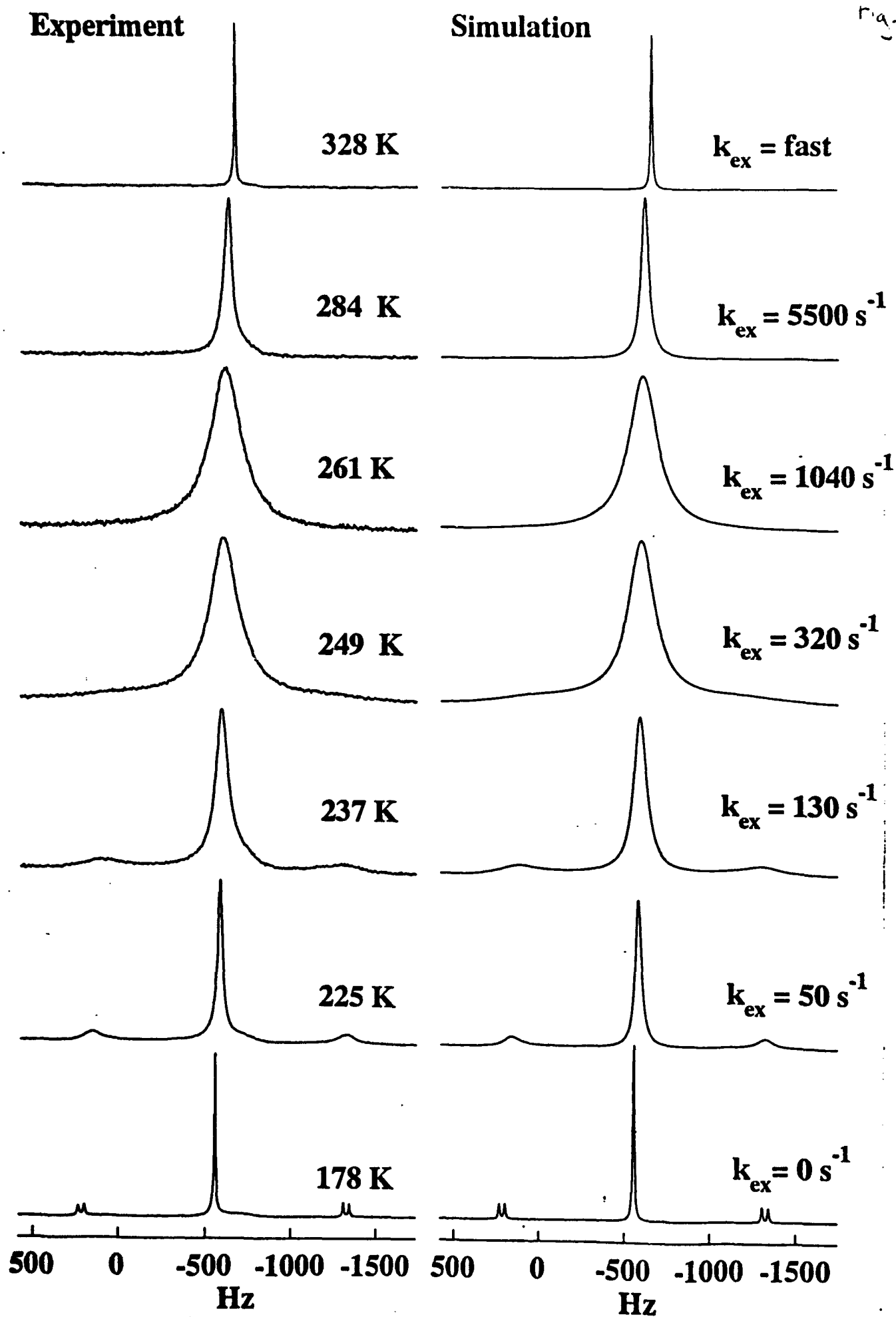
Compound	M-S (chelating)	M-S (bridging)	C-S (chelating)	C-S (bridging)	S-C-S (chelating)	S-C-S (bridging)	Ref
$[(Et_2NCS)_2Zn]_2$	2.443 2.355	2.331 2.383 2.815 2.383	1.722 1.725	1.723 1.737	117.32	117.47	[49]
$(Et_2NCS)_2Zn(TMEDA)$	2.533 2.494 2.524 2.526		1.716 1.719 1.719 1.722		117.8 117.2		[37]
$(EtNCS)_2Zn(PMe_3)$	a 2.328 b 2.329 c 2.324 2.633/2.655/2.618 2.321/2.327/2.340 2.638/2.616/2.616		a 1.707 b 1.750 c 1.731 1.690/1.690/1.723 1.722/1.731/1.730 1.706/1.697/1.711		a 118.9 b 118.4 c 118.2 118.5/118.1/116.5		This work
$[(Et_2NCS)_2Zn]_2(DEPE) \cdot 2(C_7H_8)$	2.653 2.320 2.580 2.326		1.712 1.724 1.699 1.712		117.5 118.2		[41]
$(Et_2NCS)_2CdPEt_3$	2.575 2.715 2.557 2.723		1.715 1.706 1.729 1.711		119.4 119.5		this work
$[(Et_2NCS)_2ZnMe]_2$		2.512 2.370 2.501		1.732			[34]

Table 4: TGA results for all the compounds (X = Et₂NCS₂)

Expt. No.	compound	T _{onset} ^a (°C)	weight loss		interpretation	residual weight %	
			obs'd	cal'd		obs'd	cal'd
1	(Et ₂ NCS ₂) ₂ ZnPMc ₃	100 310	17 (%) 79 (%)	21 (%) 79 (%)	loss of PMc ₃ ZnX ₂ sublimed	4 (%)	0 (%)
2	(Et ₂ NCS ₂) ₂ ZnPEt ₃	130 300	25 (%) 75 (%)	25 (%) 75 (%)	loss of PEt ₃ ZnX ₂ sublimed	0 (%)	0 (%)
3	(Et ₂ NCS ₂) ₂ CdPMc ₃	100 300	14 (%) 77 (%)	16 (%) 84 (%)	loss of PMc ₃ CdX ₂ sublimed	9 (%)	0 (%)
4	(Et ₂ NCS ₂) ₂ CdPEt ₃	280	75 (%)	73 (%)	CdX ₂ PEt ₃ decomp.	25 (%) CdS	27 (%) CdS
5	[(Et ₂ NCS ₂) ₂ Zn] ₂ depe•2C ₇ H ₈	70 290	17 (%) 67 (%)	17 (%) 66 (%)	loss of C ₇ H ₈ ZnX ₂ (μ-P) Decomp.	16 (%) ZnS	17 (%) ZnS
6	[(Et ₂ NCS ₂) ₂ Cd] ₂ depe•2C ₇ H ₈	130 310	17 (%) 65 (%)	15 (%) 61 (%)	loss of C ₇ H ₈ CdX ₂ (μ-P) Decomp.	18 (%) CdS	24 (%) CdS
7	[(Et ₂ NCS ₂) ₂ Zn _{0.5} /Cd _{0.5}] ₂ depe•2C ₇ H ₈	70 130 280	4 (%) 12 (%) 65 (%)	8 (%) 8 (%) 63 (%)	loss of C ₇ H ₈ loss of C ₇ H ₈ Zn/CdX ₂ (μ-P) Decomp.	19 (%) ZnS/CdS	21 (%) ZnS/CdS

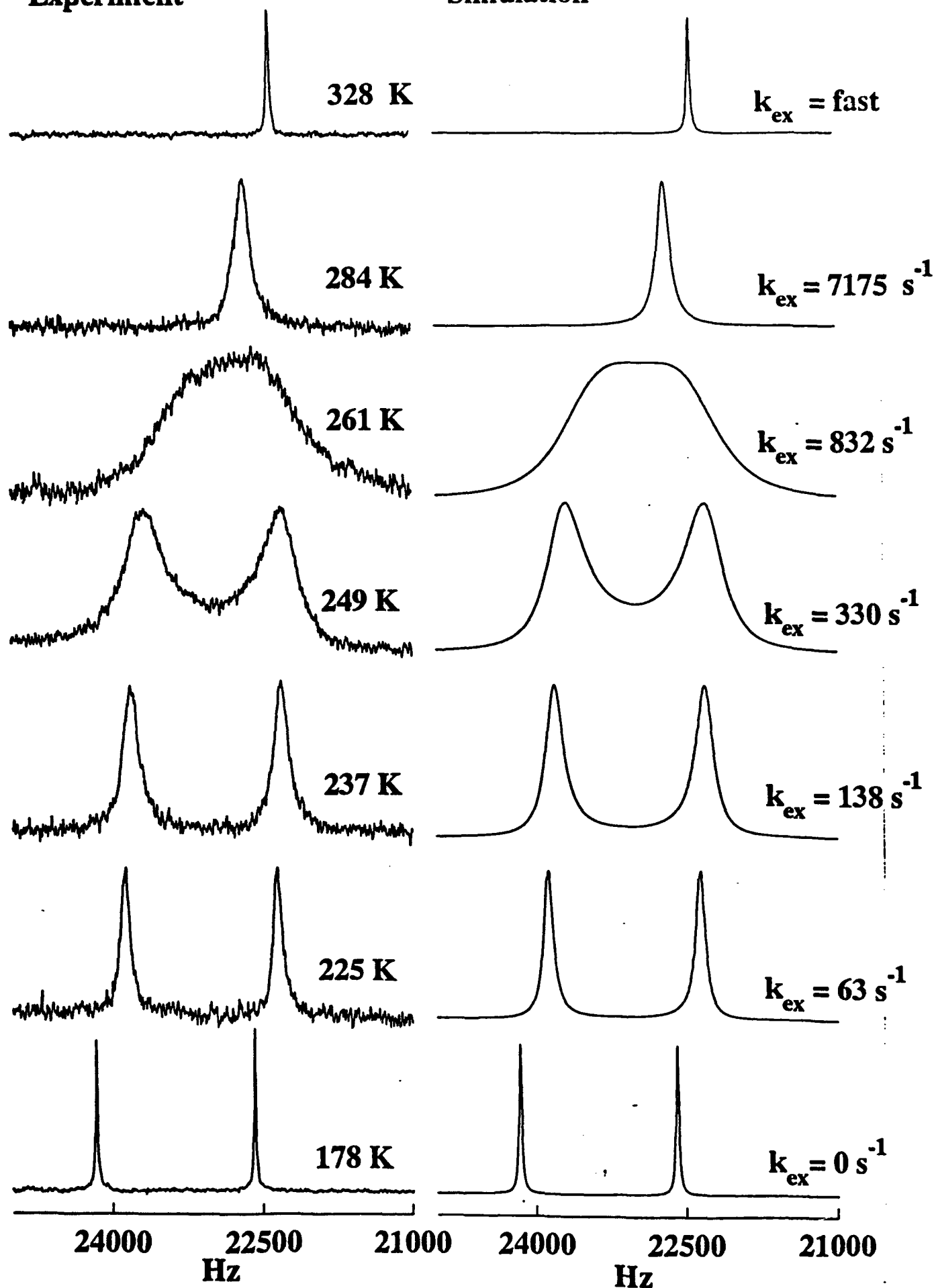
Table 5. The input and refined unit cell parameters a and c.

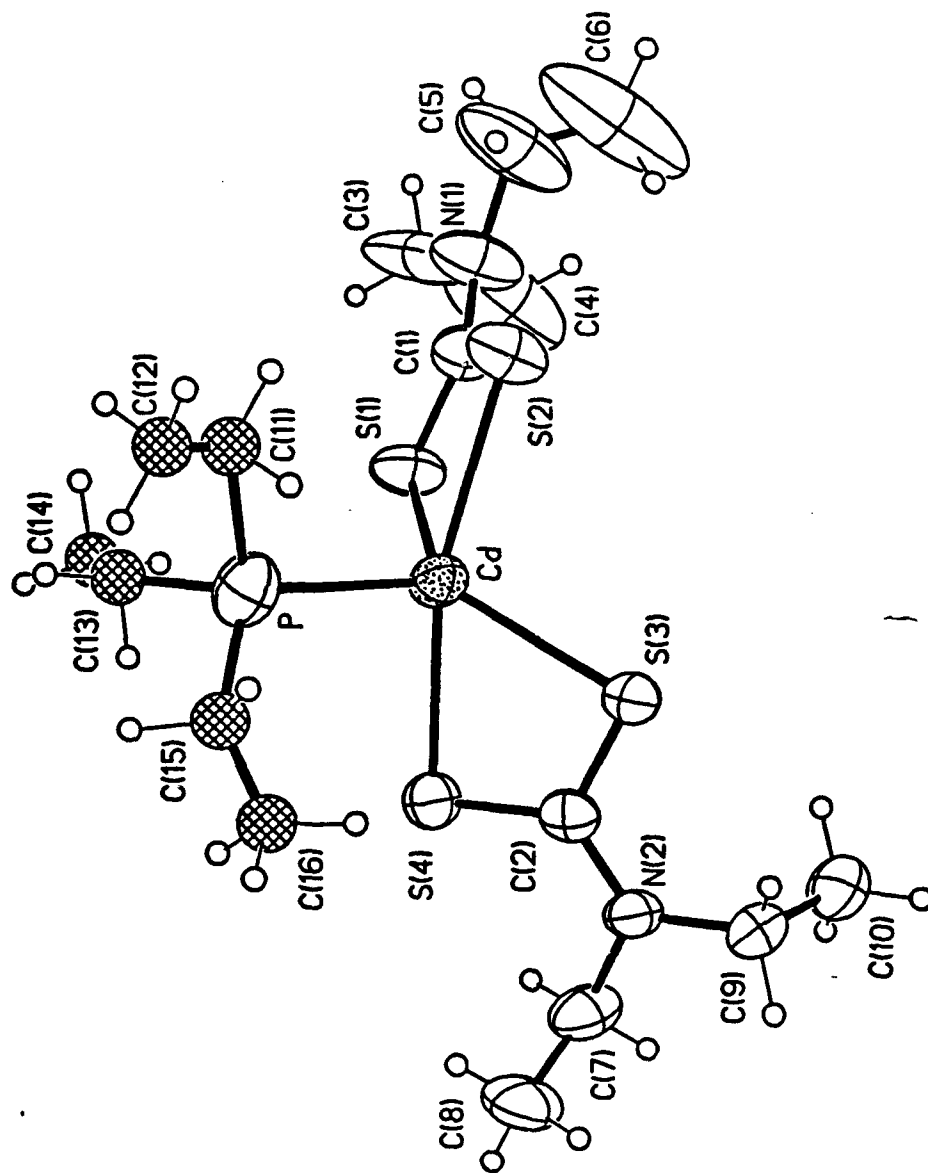
Material	Input data		Refined data	
	a (Å)	c (Å)	a (Å)	c (Å)
ZnS	3.820	6.260	3.818	6.276
Zn _{0.75} Cd _{0.25} S	3.899	6.373	3.884	6.363
Zn _{0.5} Cd _{0.5} S	3.978	6.486	3.967	6.458
Zn _{0.25} Cd _{0.75} S	4.072	6.600	4.077	6.615
CdS	4.136	6.713	4.137	6.713

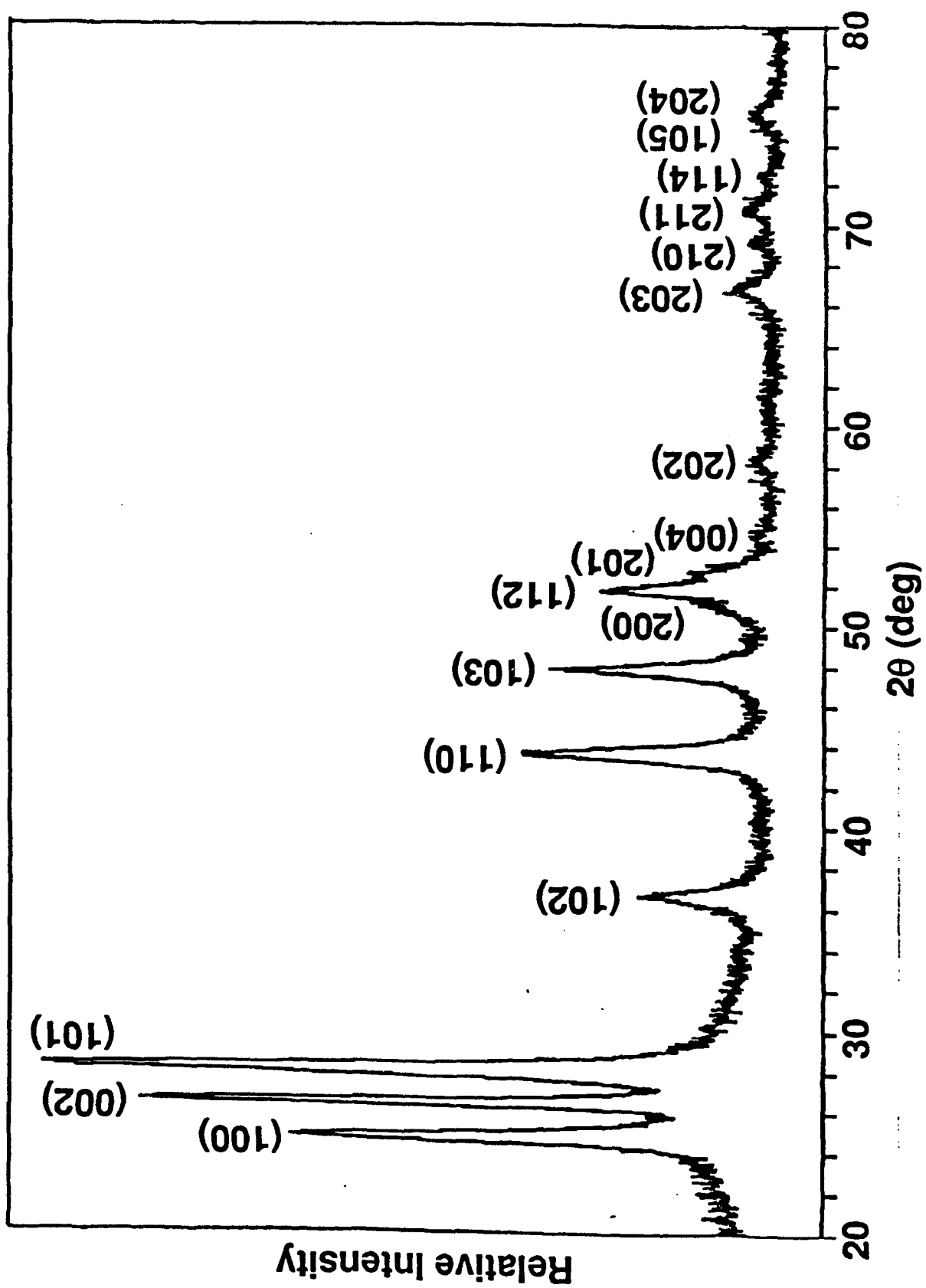


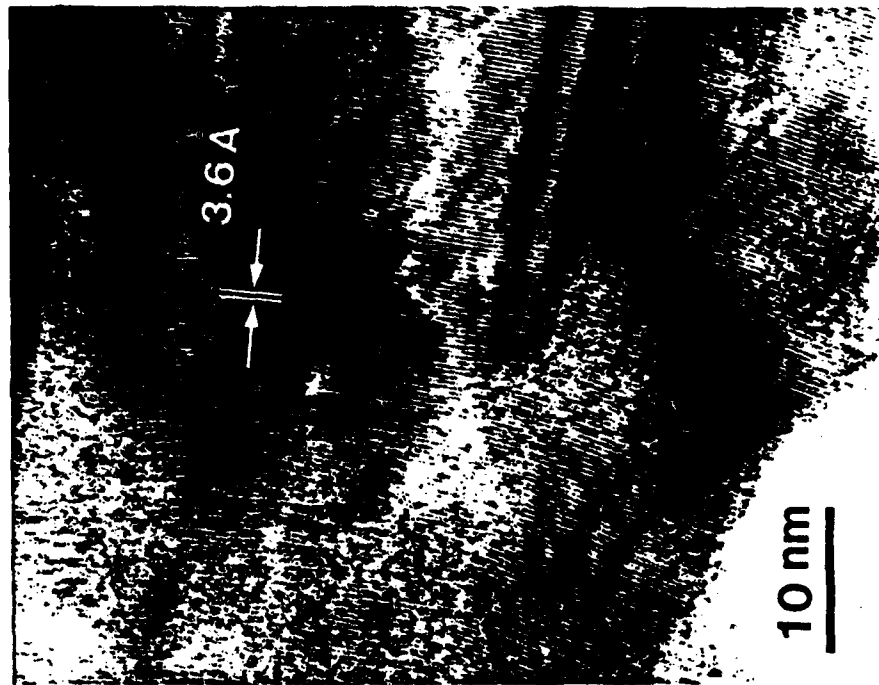
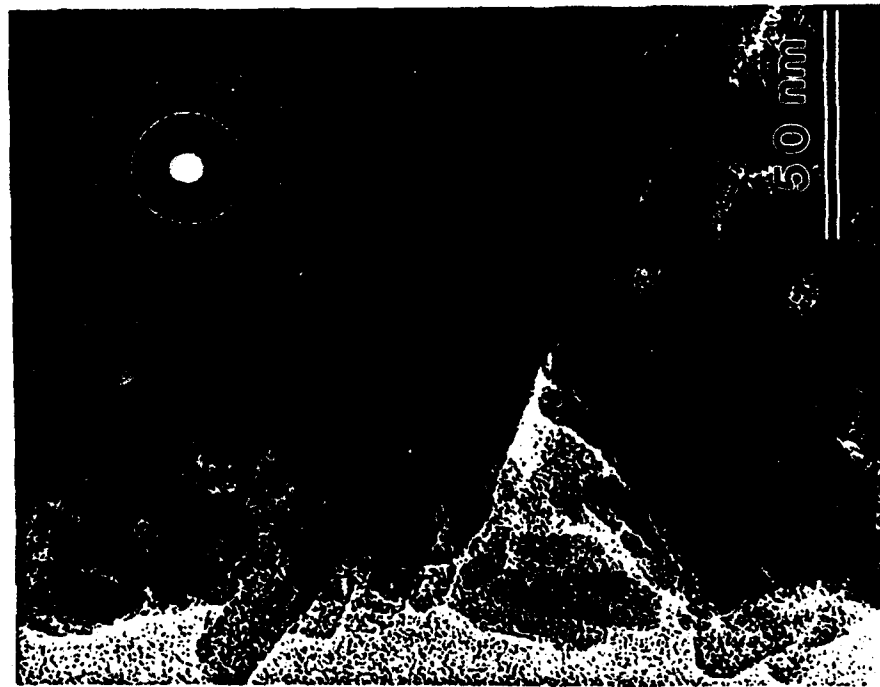
Experiment

Simulation









Crystalline CdS particles from thermal decomposition
of $(\text{Et}_2\text{NCS}_2)_2\text{Cd}(\text{PEt}_3)$

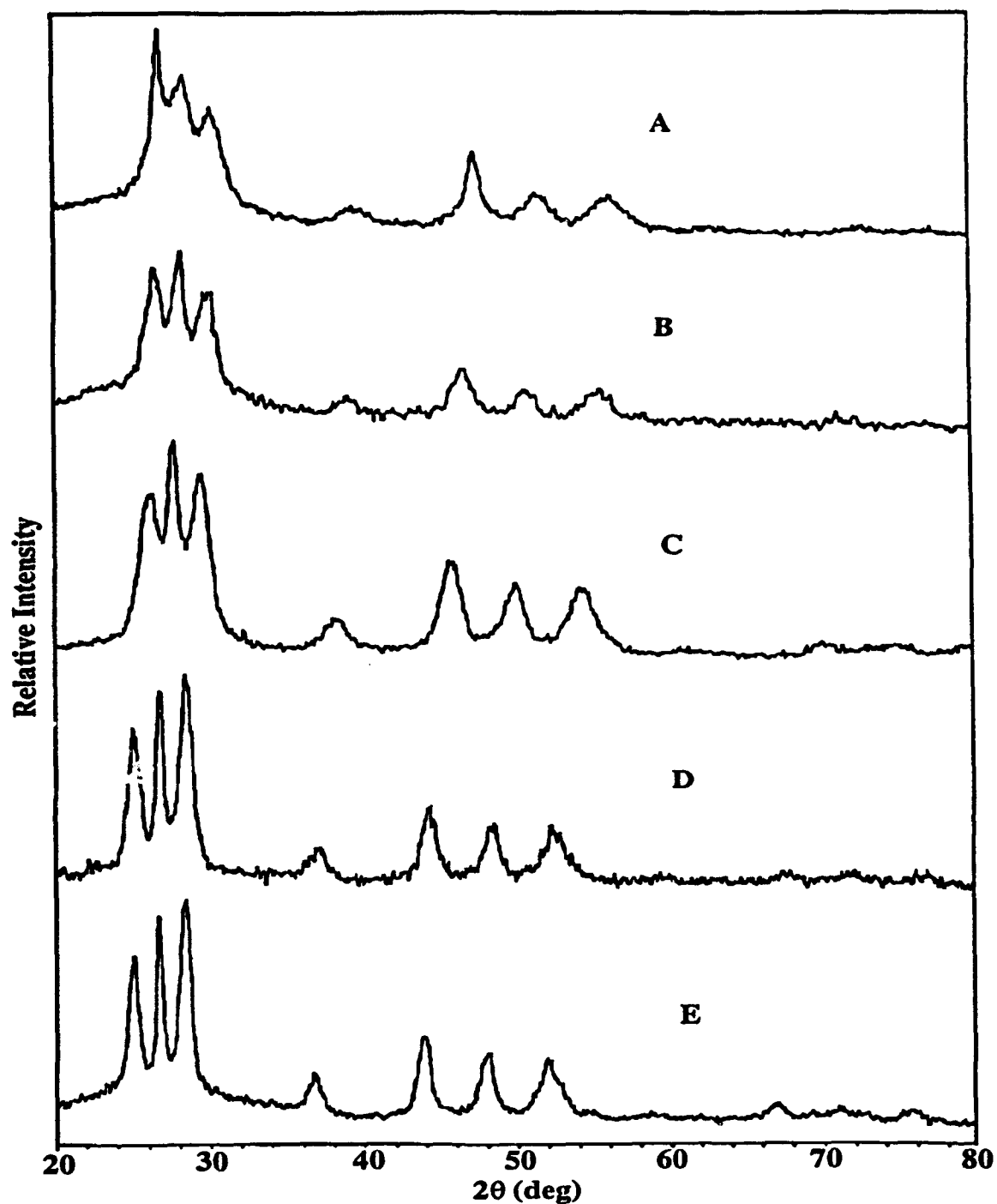


Figure 6 XRD of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ obtained from thermolysis of heterobimetallic compound, $[(\text{Et}_2\text{NCS}_2)_2\text{Zn}]_{2x}[\text{DEPE}][\text{Cd}(\text{S}_2\text{CNEt}_2)_2]_{2(1-x)}$ ($x = 1$ for A, 0.75 for B, 0.50 for C, 0.25 for D and 0 for E).